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Synthesis and Spectral Characterization of Lanthanide Complexes with Sulfamethoxazole and Their Antibacterial Activity[1]

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Abstract—A series of nonelectrolytic lanthanide(III) complexes, $[ML_2Cl_3] \cdot 2H_2O$, where M is lanthanum(III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), terbium(III), dysprosium(III), and yttrium(III), containing sulfamethoxazole ligand (L) are prepared. The structure and bonding of the ligand are studied by elemental analysis, magnetic susceptibility measurements, IR, ^{1}H NMR, *TG*/*DTA*, X-ray diffraction studies, and electronic spectra of the complexes. The stereochemistry around the metal ions is a monocapped trigonal prism in which four of the coordination sites are occupied by two each from two chelating ligands, sulfonyl oxygen, and nitrogen of the amide group and the remaining three positions are occupied by three chlorines. The ligand and the new complexes were tested in vitro to evaluate their activity against the bacteria *Escherichia coli* and *Staphylococcus aureus*.

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INTRODUCTION

The chemistry of metal complexes with heterocyclic compounds containing nitrogen, sulfur, and/or oxygen as ligand atoms has attracted increasing attention. It is well known that the heterocyclic compounds exhibit bactericidal, fungicidal, herbicidal, and insecticidal activities in addition to their application as potential drugs. Such heterocyclic ligands, when complexed with metal ions, exhibit enhanced microbiological activities [1, 2]. The role of microelements in biochemical processes is well documented [3, 4]. However, the mechanisms by which ligands operate are not common to all bioactive molecules. These molecules are expected to possess a certain ability to form complexes with particular metals. The heterofunctional biomolecules form complexes with particular metals and their salts, bringing considerable changes in the physicochemical properties of the latter [5].

The coordination behavior of ligands bearing heterocycles, especially with transition-metal ions, has been studied extensively [6–8]. Major biological interest in the complexes of these ligands stems from their suitability in designing metal-containing model systems, which mimic biologically active systems [8]. The presence of donor atoms (N, S, O) at various positions in these molecules enable them to behave as multidentate ligands and thus form chelates of diverse structural types with a wide range of metal ions. The interaction of metal ions with biomolecules and the function of metal ions in physiological systems are very complex, and the precise mechanism of these interactions is almost unknown. In the synthetic systems, ligand design based on selective complexation with metal ions is limited to ideas, such as size-matched selectivity in macrocycles, drop in stability due to increased size of chelate and steric strain. However, the ligand activity is a combination of steric, electronic, and pharmakinetic factors, and it could be understood in the light of chelation theory [5]. In this context, various heterocycles, especially azoles, occupy an important place owing to their versatile bioactivities due to the presence of multifunctional groups.

Despite their biological significance and potential applications, lanthanide complexes of these ligands have not received special attention they rightly deserve. This is because complexation of lanthanide(III) ions differs from that of *d*-block elements. The development of tailored receptors for Ln(III) remains a challenge to synthetic chemists, since lanthanide ions do not display pronounced stereochemical preferences for particular bonding modes [9]. Furthermore, lanthanide ions, in view of their electronic configuration and size, are often used as spectroscopic probe as surrogates for Ca^{2+} ion in studies of biological systems as well as promoters in dyeing industry and diagnostic agents in clinical medicine [10–12]. The aim, therefore, of the present investigation is to synthesize selected lanthanide complexes using sulfamethoxazole as a chelating agent, to

[1] The text was submitted by the authors in English.

Table 1. Analytical, conductance, and magnetic susceptibility data for the lanthanide(III) complexes

Complex*	Elemental analysis (found/calcd), %							Λ_M, mhos cm^2/mol	μ_{eff}, μ_B
	C	H	N	S	Cl	O	metal		
$[LaL_2Cl_3] \cdot 2H_2O$ (I)	32.03/	2.93/	11.21/	8.54/	14.19/	12.81/	18.53/	11.98	Dia
	31.92	2.61	11.40	8.62	14.26	13.01	18.18		
$[PrL_2Cl_3] \cdot 2H_2O$ (II)	31.94/	2.92/	11.18/	8.51	14.15/	12.77/	18.75/	11.55	3.37
	32.06	2.78	11.24	8.62	14.25	12.86	18.19		
$[NdL_2Cl_3] \cdot 2H_2O$ (III)	31.80/	2.91/	11.13/	8.48	14.09/	12.72/	19.11/	11.40	3.69
	31.46	2.88	11.24	8.64	14.28	12.66	18.84		
$[SmL_2Cl_3] \cdot 2H_2O$ (IV)	31.54/	2.89/	11.04/	8.41	13.98/	12.61/	19.76/	11.55	2.14
	31.40	2.78	11.18	8.32	14.01	12.70	19.61		
$[GdL_2Cl_3] \cdot 2H_2O$ (V)	31.26/	2.86/	10.94/	8.33	13.85/	12.50/	20.48/	11.80	7.79
	31.44	2.98	10.89	8.20	13.60	12.42	20.47		
$[TbL_2Cl_3] \cdot 2H_2O$ (VI)	31.19/	2.85/	10.91/	8.32	13.82/	12.47/	20.65/	11.66	9.96
	30.99	2.79	11.02	8.14	13.94	12.51	20.61		
$[DyL_2Cl_3] \cdot 2H_2O$ (VII)	31.13/	2.85/	10.89/	8.30	13.79/	12.45/	21.08/	11.40	10.42
	31.25	2.90	10.78	8.22	13.56	12.59	20.70		
$[YL_2Cl_3] \cdot 2H_2O$ (VIII)	34.32/	3.14/	12.01/	9.15	15.20/	13.72/	12.71/	12.12	Dia
	34.40	3.14	11.98	9.28	15.42	13.68	11.94		

* All complexes are colorless.

ascertain their bonding modes, and also to study their antibacterial activity.

EXPERIMENTAL

All reagents used were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard procedures. Lanthanum(III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), terbium(III), dysprosium(III), and yttrium(III) chlorides were obtained from Indian Rare Earths Limited, Alwaye, Kerala, South India, and all of them were used as received. The ligand sulfamethoxazole was obtained from Kerala State Drugs and Pharmaceuticals Ltd., Alleppy, Kerala, in the pure form. The compound was certified as 100% pure and, hence, used as such.

The analysis for carbon, hydrogen, and nitrogen were performed at the Central Drug Research Institute (Lucknow, India). The metal, chloride, and sulfur contents in the complexes were estimated by standard methods reported in the literature [13]. The conductance data were obtained in 10^{-3} M DMF solutions at room temperature using a Systronics direct reading digital conductivity meter-304 with a dip type conductivity cell. IR spectra were recorded in KBr pellets in the 4000–200 cm^{-1} region using a Perkin-Elmer 1600 FT-IR spectrometer. Electronic spectra were recorded in DMF solution with a Shimadzu UV–visible double beam spectrophotometer. The various bonding parameters were evaluated from the electronic spectral data as reported elsewhere [14, 15]. The ^1H NMR spectra of the ligand and its lanthanide complexes were recorded on a DPX 200 Varian Supercon NMR spectrometer using DMSO-d_6 as solvent. The room-temperature magnetic susceptibility measurements were made by the Gouy method using $Hg[Co(CNS)_4]$ as calibrant. Thermogravimetric analysis was carried out for a selected complex using Sieko (Japan, model 320) *TG*/*DTA* instrument. The X-ray diffraction patterns of the sample were recorded on a vertical-type Phillips 1130/00 X-ray diffractometer.

Synthesis of the complexes. The complexes were prepared by mixing together methanolic solutions of the appropriate lanthanide(III) chloride (1 mmol) and sulfamethoxazole (2 mmol) and refluxing the mixture for 12 h in a water bath. The reaction mixture was concentrated to 5 ml, the pH was adjusted between 9–11, and 1 ml of triethyl amine was added to yield the complex. The complex was filtered, washed with cold methanol followed by acetone, and dried in vacuo (yield 1.62 g, 64%).

RESULTS AND DISCUSSION

The ligand sulfamethoxazole, chemically known as *N′*-(5-methylisoxazol-3-yl) sulfanilamide, reacts with of lanthanum(III), praseodymium(III), neodymium(III), samarium(III), gadolinium(III), terbium(III), dysprosium(III), and yttrium(III) chlorides in a 2 : 1 molar ratio to give complexes of the type $[ML_2Cl_3] \cdot 2H_2O$.

Table 2. Prominent IR spectra bands of the ligand and its lanthanide(III) complexes (ν, cm^{-1})

Complex	NH_2 (asym.)	NH_2 (sym.)	NH	Methoxazole ring	Sulfonyl (asym. st.)	C–N aniline	C–N sulfonamide	M–O	M–N	M–Cl
I	3460	3360		1630		1270	1250	455	355	275
II	3472	3354		1640		1265	1250	450	350	285
III	3460	3360		1630		1310	1285	440	335	300
VI	3496	3346		1635		1310	1250	445	330	280
V	3420	3330		1638		1270	1280	440	350	285
VI	3400	3350		1630		1300	1285	445	350	285
VII	3408	3365		1630		1295	1250	440	335	280
VIII	3420	3340		1640		1300	1250	445	340	300
Ligand	3480	3380	3300	1635	1345	1320	1300			

The complexes are colorless, microcrystalline, and quite stable in air. The analytical data given in Table 1 for the complexes are in good agreement with the formulas proposed. A close examination of molar conductance values of the complexes (Table 1) reveals that the chelates have low conductivity, which indicates nonelectrolytic nature of the complexes.

IR spectra. The characteristic IR frequencies for the free ligand and its complexes are listed in Table 2. The free ligand shows two strong bands at 3480 and 3380 cm^{-1} corresponding to the asymmetric and symmetric stretching vibrations, respectively, of the aromatic amino group [16]. A negative shift from 20 to 70 cm^{-1} in the positions of these bands is observed in the spectra of the metal complexes. This is due to the resonance contribution from the amino group and also due to the possible hydrogen bonding interaction between the NH_2 group and sulfonyl oxygen of the neighboring molecule [17]. The strong band at 3300 cm^{-1} due to the presence of sulfonamide –NH in the IR spectrum of the ligand is absent from the spectra of the complexes, indicating the involvement of the group in chelation.

The bands at 1345 and 1170 cm^{-1} represent the asymmetric and symmetric stretching frequencies, respectively, of the sulfonyl group [16]. The absence of these bands from the spectra of the complexes indicates the linkage of the ligand to the metal ion through sulfonyl oxygen. This is also supported by the observed negative shift with respect to the band at 1170 cm^{-1}. The two strong bands at 1465 and 1380 cm^{-1} due to methoxazole ring stretching vibrations suffered no shift in the spectra of the metal complexes indicating that the methoxazole moiety is not involved in coordination [18]. A negative shift of 10–15 cm^{-1} in the stretching frequencies of the C–N band of amino and sulfonamide in the 1320 and 1300 cm^{-1} region indicates the interaction of sulfamethoxazole with the metal ion through the sulfonamide nitrogen [19].

The new bands in regions of 440–455, 335–355, and 275–300 cm^{-1} in the IR spectra of complexes are assigned to M–O, M–N, and M–Cl stretching vibrations, respectively. The absence of these bands from the spectrum of the ligand confirms the bonding of the metal ion through the sulfonyl oxygen, amido nitrogen, and chloride ions in the lanthanide sulfamethoxazole chelates [20]. The presence of water molecules outside the coordination sphere is indicated by a broad band in the region of 3500–3550 cm^{-1}. This is further confirmed by the appearance of rocking vibrational mode of water molecules [19].

Electronic spectra. The electronic spectral data of lanthanide(III) chlorides, the ligand, and its complexes along with various bonding parameters evaluated from the spectral data to understand the nature and strength of the metal–ligand bond, are given in Table 3. The electronic spectrum of the ligand showed n–π* and π–π* transitions at 33 333 and 37 364 cm^{-1}, respectively. Complex formation with metal ions resulted in a hypsochromic shift of these bands. The absorption bands of praseodymium(III), neodymium(III), and samarium(III) in the UV and visible region appear due to transitions from the ground levels $^3H_4$, $^4I_{9/2}$, and $^6H_{5/2}$, respectively, to the excited J levels of $4f$ configuration [21]. The sharp bands due to f–f transition originating within the $4f^n$ configuration of lanthanide ions are only slightly affected by the immediate surrounding of the metal ion, and this is commonly attributed to the shielded nature of the $4f$ orbitals by the overlying $5s^2$ and $5p^6$ orbitals. However, the shift to lower frequency region can be concluded as due to complex formation [22].

A close examination of the data in Table 3 reveals that the positive values of the bonding parameter ($b^{1/2}$) are indicative of covalent character of the metal–ligand bond in the complexes [23]. This is further supported by oscillator strength (f) values for the complexes [24]. The shapes of hypersensitive transitions of the complexes closely resemble that of the seven coordinated

Table 3. Electronic spectral data (cm^{-1}) and related bonding parameters

λ_{max}		Energy level assignment	ε_{max}	β	$b^{1/2}$	δ, %	$f \times 10^{-3}$
$LnCl_3$	complex						
$PrCl_3$	$[PrL_2Cl_3] \cdot 2H_2O$						
22.471	22.300	$^3H_4 \longrightarrow {}^3P_2$	980.6	0.9924	0.06124	0.7557	14.96
21.276	21.100	$\longrightarrow {}^3P_1$	682.9	0.9915	0.06480	0.8545	10.42
20.830	20.680	$\longrightarrow {}^3P_0$	403.2	0.9928	0.05999	0.7252	6.15
16.949	16.800	$\longrightarrow {}^1D_2$	330.6	0.9912	0.06633	0.8878	5.05
$NdCl_3$	$[NdL_2Cl_3] \cdot 2H_2O$						
19.608	19.520	$^4I_{9/2} \longrightarrow {}^4G_{9/2}$	1007.8	0.9955	0.04743	0.4520	15.38
17.241	17.177	$\longrightarrow {}^4G_{5/2}, {}^2G_{7/2}$	1617.9	0.9963	0.04301	0.3714	24.69
14.705	14.672	$\longrightarrow {}^4F_{9/2}$	423.1	0.9978	0.03316	0.2205	6.46
13.514	13.487	$\longrightarrow {}^2S_{3/2}, {}^4F_{7/2}$	1434.6	0.9981	0.03082	0.1904	21.89
12.500	12.420	$\longrightarrow {}^4F_{5/2}$	1422.0	0.9936	0.05656	0.6441	21.70
$SmCl_3$	$[SmL_2Cl_3] \cdot 2H_2O$						
26.667	26.540	$^6H_{5/2} \longrightarrow {}^6P_{3/2}$	1363.5	0.9952	0.04899	0.4823	22.09
24.691	24.480	$\longrightarrow {}^4F_{9/2}$	410.7	0.9915	0.06519	0.8573	6.49
24.096	23.896	$\longrightarrow {}^4P_{5/2}$	1549.7	0.9917	0.06442	0.8369	24.69
21.739	21.547	$\longrightarrow {}^4I_{13/2}$	310.4	0.9912	0.06633	0.8878	5.13
20.833	20.716	$\longrightarrow {}^4I_{11/2}$	1389.2	0.9944	0.05291	0.5632	21.41

complexes [25], suggesting the coordination number seven around the metal ion in these complexes.

Magnetic susceptibility. The magnetic susceptibility values (Table 1) of the complexes reveal that the lanthanum(III) and yttrium(III) complexes are diamagnetic, while all others are paramagnetic. The magnetic susceptibilities of all the paramagnetic complexes, except that of samarium, showed slight deviation from the van Vleck values [26], indicating an insignificant participation of the 4*f* electrons in the bonding, since these are well shielded by $5s^2\ 5p^6$ octet. The relatively high value obtained in the case of the samarium complex is due to the fact that the energy difference between the ground state and the next higher level is of an order of *kT*, which leads to the thermal population of high-energy levels and show susceptibilities due to the first-order Zeeman effect [27].

NMR spectra. In the ^1H NMR spectrum of the ligand, the singlet observed at δ 10.50 ppm may be assigned to the sulfonamide proton. This signal is absent from the spectrum of the diamagnetic lanthanum(III) complex indicating the involvement of sulfonamide nitrogen in chelation after deprotonation [28]. In the spectrum of the lanthanum(III) complex, signals due to phenyl ring protons (two sets of doublets at δ 6.7 and 7.4 ppm correspond to protons at the C-3, C-5 and C-2, C-6 positions, respectively) and methoxazole moiety protons (two sets of singlets at δ 3.48 and 3.00 ppm correspond to protons at the C-5 and C-2 positions, respectively) do not exhibit any shift in their position. This suggests that metal–ligand interactions are very weak and do not alter the electronic environment around these positions, which are only a few bonds away from the metal ion.

Thermal analysis. Thermal studies are carried out on a typical complex, viz., lanthanum(III)–sulfamethoxazole with a view to understand the decomposition pattern of the complexes. The *TG* and *DTA* curves for the complex are given in Fig. 1. The complex was heated in static air at a rate of 5 K/min. The chelate first showed an endothermic decomposition at 115.57°C due to the loss of water of hydration as indicated by the endothermic *DTA* curve [29]. The complex was found to decompose exothermally above 270.2°C

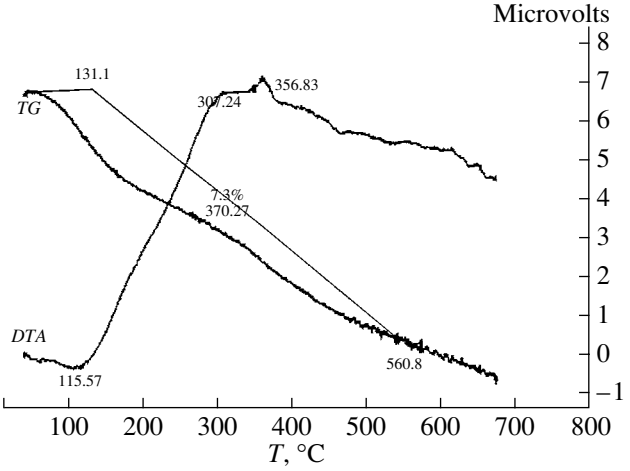
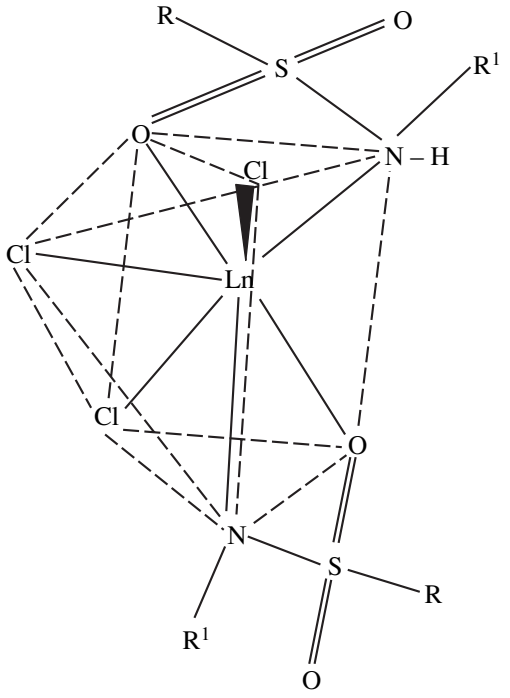


Fig. 1. Thermogram of lanthanum(III)–sulfamethoxazole complex.



Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Y;

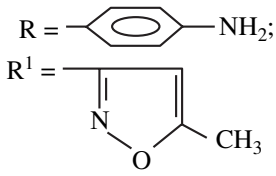


Fig. 2. Lanthanide(III)–sulfamethoxazole complex.

with a weight loss of 7.3% due to the organic moiety. The exothermic curve at 358.93°C with a weight loss of 27.39% is due to the loss of three chloride ions [30]. The stable residue formed at 560.8°C is due to the formation of stable lanthanum oxide [31].

X-ray diffraction. Our efforts to prepare single crystals of these complexes were unsuccessful due to a high molecular mass of the metal ions involved. Therefore, powder X-ray diffraction patterns have been recorded. The diffraction patterns reveal the crystalline nature of the complex. Attempts to index the diffraction patterns using autoindexing computer programs have failed to yield acceptable unit-cell parameters in crystal systems of the complexes. This was ascribed due to the large size of the chelate molecules resulting in a reasonably bigger unit cell and symmetry arrangements.

The foregoing results obtained lead to the conclusion that sulfamethoxazole acts as a bidentate ligand complexing the metal ion through the sulfonyl oxygen and nitrogen of the amide group. The metal ion acquires a coordination number of seven. Based on the physicochemical and spectral data obtained, a monocapped trigonal prism geometry, as shown in Fig. 2, was proposed for the lanthanide(III) complexes of sulfamethoxazole.

Antibacterial activity. The ligand, sulfamethoxazole, and its lanthanide(III) complexes were tested for the in vitro growth inhibitory activity against bacteria *Escherichia coli* and *Staphylococcus aureus*. The bacteria were cultured in nutrient agar medium and used as inoculums for the study. The percentage of bacterial growth inhibition produced by the complexes was esti-

Table 4. Antibacterial activity of the lanthanide complexes

Complex	Percentage of inhibition to bacterial growth					
	0 h	2 h	4 h	6 h	8 h	24 h
Against *Staphylococcus aureus*						
Ligand	8.1	10.2	16.3	16.4	22.4	44.1
I	13.6	15.0	21.2	26.8	41.5	70.4
II	13.9	16.3	22.4	26.7	42.8	90.0
III	17.4	18.1	35.5	40.0	68.3	90.2
IV	22.2	29.6	33.5	56.1	62.5	85.5
V	14.2	18.4	33.0	43.2	46.5	88.4
VI	20.1	37.1	50.8	54.3	70.0	90.2
VII	18.6	26.5	31.7	42.2	47.0	54.4
VIII	17.4	24.1	30.8	32.9	48.2	54.3
Against *Escherichia coli*						
Ligand	11.4	22.4	44.0	56.2	68.1	89.2
I	8.1	13.5	16.2	22.3	41.5	54.8
II	4.3	11.6	16.4	26.8	44.1	57.6
III	7.7	15.0	26.7	30.8	47.5	59.1
IV	6.4	14.1	25.1	31.1	48.1	55.4
V	6.1	15.2	26.1	32.2	42.2	50.2
VI	7.3	18.1	29.1	37.1	44.1	53.1
VII	4.1	11.2	25.8	30.6	39.8	42.2
VIII	4.7	12.1	29.7	37.2	40.1	44.1

mated by serial dilution technique [32] by employing a 10^{-6} M solution of the complexes prepared in DMF.

The results (Table 4) showed that lanthanide–sulfamethoxazole complexes are more toxic against gram-positive organism, namely *Staphylococcus aureus*, than the gram-negative organism, *Escherichia coli*. The ligand showed an activity of 44.17% of bacterial growth inhibition, while the metal chelates produced 54.3–90.2% of bacterial growth inhibition against the gram-positive organism. However, in the antibacterial activity against *Escherichia coli*, the ligand exhibited activity of 89.2%, while that of its lanthanide complexes were of the order of 42.2–59.1%.

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